Synthesis of Benzazetine Derivatives by Intramolecular Iodoamination of *o*-(Acylamino)styrene Derivatives

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The iodoamination of *o*-(acylamino)styrene derivatives using iodine and sodium hydrogencarbonate, producing 7-acyl-8-iodomethylbicyclo[4.2.0]-7-azaoct-1,3,5-triene [1-acyl-2-(iodomethyl)benzazetine] derivatives, is described. Replacement of the iodo moiety by hydrogen or phenylthio group is also reported.

The intramolecular haloamination reaction has been used widely for the preparation of nitrogen heterocyclic compounds.¹ We investigated the potential of iodoamination in the construction of benzazetine derivatives, and found that 1-acyl-2-(iodomethyl)benzazetine derivatives could be synthesized by treating *o*-(acylamino)styrene derivatives with I₂/NaHCO₃.^{2,3} Benzazetine derivatives have received attention as potential precursors for the generation of *o*-quinonemethide monoimine intermediates.⁴ Although several reports on the formation of benzazetine derivatives have appeared,⁵ few general synthetic methods of this class of molecules have been developed.⁶ Herein, we wish to report on the results of our investigation, which offer simple access to the construction of benzazetine derivatives.

The intramolecular iodoamination of o-(acylamino)styrene derivatives 1 could be easily achieved, as illustrated in Scheme 1. Thus, the reaction of 1 with 3 equivalents each of iodine and sodium hydrogencarbonate in acetonitrile at 0 °C proceeded smoothly to afford the 2-(iodomethyl)benzazetine derivatives 2 in good yields. In order to confirm the (iodomethyl)benzazetine structure of 2, replacement of the iodine of 2 by hydrogen was tried. The treatment of 2 with tributyltin hydride at room temperature gave 2-methylbenzazetine derivatives 3 in good yields. The possibility of the dihydroindole structure of the products was excluded by these results. The benzazetine structure was further confirmed by a FAB-mass spectral analysis of 2a, excluding the possibility of the symmetrical dimer structure (see Experimental).

The nucleophilic substitution of the iodine of **2** was performed using sodium benzenethiolate, generated from benzenethiol and sodium hydride, in DMF at 0 $^{\circ}$ C to give 2-(phenylthiomethyl)benzazetine derivatives **4** in satisfactory yields, as shown in Scheme 2.

In summary, we have shown that iodoamination of *o*-(acylamino)styrene derivatives can offer a simple method for constructing benzazetine derivatives. The ready availability of the starting materials and the ease of operation make the present method attractive.

Experimental

General. The melting points were determined on a Laboratory Devices MEL-TEMP II melting-point apparatus and are uncor-

NHCOR³ 1 CH₂ I2, NaHCO NCOR³ MeCN. 0 °C 2a 88%; 2b 89%; 2c 96% 2d 78%; 2e 85%; 2f 93% R^1 n-Bu₃SnH Me benzene, rt NCOR³ 3a 85%; 3b 81%; 3c 95% 3d 88%; 3e 60%; 3f 94% **a** $R^1 = Me$, $R^2 = H$, $R^3 = Me$ **b** R^1 = Me, R^2 = H, R^3 = CF₃ **c** $R^1 = Me_1 R^2 = H_1 R^3 = Ph_2$ **d** $R^1 = Ph, R^2 = H, R^3 = Me$ **e** $R^1 = Ph, R^2 = H, R^3 = CF_3$ $\mathbf{f} \mathbf{R}^1 = \mathbf{Ph}, \mathbf{R}^2 = \mathbf{Cl}, \mathbf{R}^3 = \mathbf{Me}$ Scheme 1. Me hSH. NaH CH₂SPh DMF 0 NCOR 4a R = Me 55%

4a R = Me 55% 4c R = Ph 66%

Scheme 2.

rected. The IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. The ¹H NMR spectra were determined using SiMe₄ as an internal reference in CDCl₃ with a JEOL JNM-GX270 FT NMR spectrometer operating at 270 MHz, or a JEOL ECP500 FT NMR spectrometer operating at 500 MHz. The ¹³C NMR spectrum was determined using SiMe₄ as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz in CDCl₃. Low-resolution mass spectra (EI) were recorded on a JEOL AUTOMASS 20 spectrometer (Center for Joint Research

and Development, this University). The FAB mass spectrum was recorded using a xenone ionization technique with *m*-nitrobenzyl alcohol as the matrix on a JEOL JMS-AX505 HA spectrometer (Faculty of Agriculture, this University). Thin-layer chromatography (TLC) was carried out on Merck Kieselgel 60 PF₂₅₄. All of the solvents used were dried over appropriate drying agents and distilled under argon prior to use. All of the reactions were carried out under argon.

Starting Materials. N-[2-(1-Methylethenyl)phenyl]acetamide (1a) and N-[2-(1-methylethenyl)phenyl]trifluoroacetamide (1b) were prepared by the action of acetic anhydride and trifluoroacetic anhydride, respectively, upon 2-(1-methylethenyl)aniline in pyridine. 1a: 92%; mp 49–51 °C (hexane–Et₂O) (lit.⁷ 52 °C). 1b: 97%; mp 59-60 °C (hexane); IR (KBr disk) 3266 and 1702 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 2.10 (3H, s), 5.06 (1H, s), 5.48 (1H, s), 7.15–7.4 (3H, m), 8.27 (1H, d, J = 8.2 Hz), and 8.48 (1H, br s). Found: C, 57.48; H, 4.41; N, 6.08%. Calcd for C11H10F3NO: C, 57.64; H, 4.40; N, 6.11%. N-[2-(1-Methylethenyl)phenyl]benzamide (1c) was prepared according to a reported procedure.⁸ N-[2-(1-Phenylethenyl)phenyl]acetamide (1d) and N-[2-(1-phenylethenyl)phenyl]trifluoroacetamide (1e) were prepared by the action of acetic anhydride and trifluoroacetic anhydride, respectively, upon 2-(1-phenylethenyl)aniline^{3g,9} in pyridine. 1d: 94%; mp 126–128 °C (hexane–CH₂Cl₂) (lit.¹⁰ 123–125 °C). 1e: 95%; mp 56-59 °C (hexane-Et₂O); IR (KBr disk) 3386 and 1732 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 5.40 (1H, d, J = 1.0Hz), 5.91 (1H, d, J = 1.0 Hz), 7.25–7.4 (7H, m), 7.45 (1H, td, J = 7.3, 1.6 Hz), 7.81 (1H, br s), and 8.17 (1H, dd, J = 8.2, 1.3Hz). Found: C, 65.84; H, 4.21; N, 4.64%. Calcd for C₁₆H₁₂F₃NO: C, 65.98; H, 4.15; N, 4.81%. N-[4-Chloro-2-(1-phenylethenyl)phenyl]acetamide (1f) was prepared from 2-amino-5-chlorobenzophenone as follows. The action of MeMgBr on 2-amino-5-chlorobenzophenone in Et2O at 0 °C gave 1-(2-amino-5-chlorophenyl)-1-phenylethanol: 86%; mp 97-100 °C (hexane-Et₂O); IR (KBr disk) 3455, 3359, and 1607 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 1.86 (3H, s), 3.67 (3H, br), 6.55 (1H, d, J = 8.6 Hz), 7.08 (1H, dd, J = 8.6, 2.3 Hz), and 7.2–7.4 (6H, m). Found: C, 67.82; H, 5.90; N, 5.41%. Calcd for C14H14CINO: C, 67.88; H, 5.70; N, 5.65%. This amino alcohol was heated at 250 °C (no solvent) according to the procedure developed by Smith and Livinghouse¹¹ to give 4-chloro-2-(phenylethenyl)aniline: 82%; R_f 0.68 (1:2 EtOAc-hexane); IR (neat) 3471, 3383, and 1614 cm^{-1} ; ¹H NMR (270 MHz, CDCl₃) δ 3.54 (2H, br), 5.35 (1H, d, J =1.0 Hz), 5.80 (1H, d, J = 1.0 Hz), 6.60 (1H, d, J = 8.9 Hz), 7.10 (1H, dd, J = 8.9, 2.3 Hz), and 7.25–7.4 (6H, m). Found: C, 73.12; H, 5.38; N, 6.25%. Calcd for C₁₄H₁₂ClN: C, 73.20; H, 5.27; N, 6.10%. This aminostyrene was acetylated with Ac₂O in pyridine to give 1f: 90%; mp 134-136 °C (hexane-Et₂O); IR (KBr disk) 3219 and 1661 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.79 (3H, s), 5.39 (1H, s), 5.89 (1H, s), 6.90 (1H, br s), 7.29-7.38 (7H, m), and 8.14 (1H, d, J = 8.7 Hz). Found: C, 70.91; H, 5.29; N, 4.99%. Calcd for C₁₆H₁₄ClNO: C, 70.72; H, 5.19; N. 5.15%.

7-Acetyl-8-iodomethyl-8-methylbicyclo[4.2.0]-7-azaoct-1,3, 5-triene (2a). Typical Procedure for the Iodoamination of 1: To a stirred solution of 1a (0.21 g, 1.2 mmol) in MeCN (15 mL) containing NaHCO₃ (0.30 g, 3.6 mmol) at 0 °C was added I₂ (0.91 g, 3.6 mmol) portionwise. After stirring was continued for 1 h, 10% aqueous Na₂S₂O₃ (15 mL) was added. Acetonitrile was evaporated and the resulting mixture was extracted with Et₂O three times (10 mL each). The combined extracts were washed with saturated aqueous NaHCO₃ and then brine, and dried over anhydrous K₂CO₃. After evaporation of the solvent the residue was purified by preparative TLC on SiO₂ to give **2a** (0.30 g, 82%); mp 70–72 °C (hexane–Et₂O); IR (KBr disk) 1645 and 1601 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 1.81 (3H, s), 2.17 (3H, s), 3.39 (1H, d, J = 10.9 Hz), 3.58 (1H, d, J = 10.9 Hz), 7.08 (1H, dd, J = 7.6, 1.6 Hz), 7.1–7.25 (2H, m), and 7.29 (1H, td, J = 7.6, 1.6 Hz); ¹³C NMR (125 MHz) δ 16.19, 21.80, 26.47, 77.28, 122.88, 124.57, 126.31, 126.50, 129.34, 138.16, and 159.41; MS (EI) m/z (%) 301 (M⁺, 8.4) and 160 (100); FAB-MS m/z 302.0 [(M + 1)⁺]. Found: C, 44.18; H, 4.16; N, 4.61%. Calcd for C₁₁H₁₂INO: C, 43.87; H, 4.02; N, 4.65%.

8-Iodomethyl-8-methyl-7-trifluoroacetylbicyclo[4.2.0]-7-azaoct-1,3,5-triene (2b): R_f 0.48 (1:4 AcOEt-hexane); IR (neat) 1668 and 1605 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 1.92 (3H, s), 3.53 (1H, d, J = 11.2 Hz), 3.60 (1H, d, J = 11.2 Hz), 7.12 (1H, dd, J = 7.6, 1.6 Hz), and 7.25–7.45 (3H, m); MS (EI) m/z(%) 355 (M⁺, 7.0) and 214 (100). Found: C, 36.87; H, 2.78; N, 3.54%. Calcd for C₁₁H₉F₃INO: C, 37.21; H, 2.55; N, 3.94%.

7-Benzoyl-8-iodomethyl-8-methylbicyclo[4.2.0]-7-azaoct-1,3, 5-triene (2c): mp 98–101 °C (hexane–Et₂O); IR (KBr disk) 1624 and 1599 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.94 (3H, s), 3.49 (1H, d, J = 11.0 Hz), 3.67 (1H, d, J = 11.0 Hz), 7.18 (1H, dd, J = 7.8, 0.9 Hz), 7.23 (1H, ddd, J = 8.7, 7.8, 2.3 Hz), 7.33–7.39 (2H, m), 7.45–7.49 (2H, m), 7.51 (1H, tt, J = 7.3, 2.3 Hz), and 8.25 (2H, dd, J = 7.3, 2.3 Hz); MS (EI) m/z (%) 363 (M⁺, 14) and 222 (100). Found: C, 52.92; H, 3.84; N, 3.86%. Calcd for C₁₆H₁₄INO: C, 52.91; H, 3.89; N, 3.86%.

7-Acetyl-8-iodomethyl-8-phenylbicyclo[**4.2.0**]-**7-azaoct-1,3, 5-triene (2d):** mp 132–134 °C (hexane–CH₂Cl₂); IR (KBr disk) 1638 and 1595 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 2.24 (3H, s), 3.90 (2H, s), 7.03 (1H, dd, J = 7.6, 1.6 Hz), 7.20 (2H, t, J = 7.6 Hz), and 7.3–7.4 (6H, m); MS (EI) m/z (%) 363 (M⁺, 7.7) and 222 (100). Found: C, 52.55; H, 4.03; N, 4.01%. Calcd for C₁₆H₁₄INO: C, 52.91; H, 3.89; N, 3.86%.

8-Iodomethyl-8-phenyl-7-trifluoroacetylbicyclo[**4.2.0**]**-7-azaoct-1,3,5-triene (2e):** mp 109–111 °C (hexane–Et₂O); IR (KBr disk) 1668 and 1602 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 3.93 (1H, d, J = 11.9 Hz), 4.02 (1H, d, J = 11.9 Hz), 7.15 (1H, dd, J = 7.6, 1.6 Hz), and 7.3–7.5 (8H, m); MS (EI) m/z (%) 417 (M⁺, 24), 320 (39), and 193 (100). Found: C, 46.35; H, 2.95; N, 3.33%. Calcd for C₁₆H₁₁F₃INO: C, 46.07; H, 2.66; N, 3.36%.

7-Acetyl-3-chloro-8-iodomethyl-8-phenylbicyclo[4.2.0]-7-azaoct-1,3,5-triene (2f): mp 74–75 °C (hexane–Et₂O); IR (KBr disk) 1643 and 1600 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.24 (3H, s), 3.86 (1H, d, J = 11.9 Hz), 3.88 (1H, d, J = 11.9 Hz), 6.98 (1H, d, J = 2.3 Hz), 7.13 (1H, d, J = 8.2 Hz), 7.29 (1H, dd, J = 8.2, 2.3 Hz), and 7.34–7.41 (5H, m); MS (EI) m/z (%) 397 (M⁺, 5.6) and 256 (100). Found: C, 48.19; H, 3.31; N, 3.40%. Calcd for C₁₆H₁₃CIINO: C, 48.33; H, 3.30; N, 3.52%.

7-Acetyl-8,8-dimethylbicyclo[**4.2.0**]-**7-azaoct-1,3,5-triene** (**3a**). A solution of **2a** (0.16 g, 0.52 mmol) in benzene (3 mL) containing *n*-Bu₃SnH (0.29 g, 1.0 mmol) was stirred at room temperature for 1 h. The solvent was evaporated to give a residue, which was chromatographed on SiO₂ (3:1 hexane–AcOEt) to give **3a** (77 mg, 85%); R_f 0.39 (1:3 AcOEt–hexane); IR (neat) 1643 and 1603 cm⁻¹; ¹HNMR (270 MHz, CDCl₃) δ 1.61 (6H, s), 2.11 (3H, s), 7.07 (1H, dd, J = 7.6, 1.3 Hz), 7.10 (1H, dd, J = 7.6, 1.3 Hz), 7.10 (1H, dd, J = 7.6, 1.3 Hz); MS (EI) m/z (%) 175 (M⁺, 38) and 160 (100). Found: C, 75.28; H, 8.07; N, 7.80%. Calcd for C₁₁H₁₃NO: C, 75.40; H, 7.48; N, 7.99%.

8,8-Dimethyl-7-trifluoroacetylbicyclo[4.2.0]-7-azaoct-1,3,5-

triene (3b). A similar reaction of **2b** with *n*-Bu₃SnH at room temperature for 6 h gave **3b**: R_f 0.50 (1:4 AcOEt–hexane); IR (neat) 1666 and 1607 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 1.71 (6H, s), 7.1–7.15 (1H, m), and 7.25–7.35 (3H, m); MS (EI) m/z (%) 229 (M⁺, 61) and 214 (100). Found: C, 57.58; H, 4.09; N, 5.99%. Calcd for C₁₁H₁₀F₃NO: C, 57.64; H, 4.40; N, 6.11%.

7-Benzoyl-8,8-dimethylbicyclo[**4.2.0**]-**7-azaoct-1,3,5-triene** (**3c**). A similar reaction of **2c** with *n*-Bu₃SnH at room temperature for 10 min gave **3c**: R_f 0.71 (1:3 AcOEt–hexane); IR (neat) 1622 and 1599 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.72 (6H, s), 7.14–7.22 (2H, m), 7.28–7.33 (2H, m), 7.45 (2H, t, J = 7.3Hz), 7.49 (1H, tt, J = 7.3, 1.3 Hz), and 8.15 (2H, dd, J = 7.3, 1.3 Hz); MS (EI) m/z (%) 237 (M⁺, 34) and 222 (100). Found: C, 80.95; H, 6.27; N, 5.75%. Calcd for C₁₆H₁₅NO: C, 80.98; H, 6.37; N, 5.90%.

7-Acetyl-8-methyl-8-phenylbicyclo[**4.2.0**]-**7-azaoct-1,3,5-triene (3d).** A similar reaction of **2d** with *n*-Bu₃SnH at room temperature overnight gave **3d**: mp 60–62 °C (pentane); IR (KBr disk) 1643 and 1599 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 1.98 (3H, s), 2.22 (3H, s), 7.03 (1H, dd, J = 7.6, 1.3 Hz), 7.1–7.2 (2H, m), and 7.25–7.35 (6H, m); MS (EI) *m/z* (%) 237 (M⁺, 60), 222 (82), and 194 (100). Found: C, 80.64; H, 6.56; N, 5.83%. Calcd for C₁₆H₁₅NO: C, 80.98; H, 6.37; N, 5.90%.

8-Methyl-8-phenyl-7-trifluoroacetylbicyclo[4.2.0]-7-azaoct-1,3,5-triene (3e). A similar reaction of 2e with *n*-Bu₃SnH at room temperature overnight gave 3e: mp 70–75 °C (pentane); IR (KBr disk) 1663 and 1604 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 2.08 (3H, s), 7.07 (1H, dd, J = 7.3, 1.3 Hz), and 7.25–7.4 (8H, m); MS (EI) m/z (%) 291 (M⁺, 100). Found: C, 66.11; H, 4.24; N, 4.65%. Calcd for C₁₆H₁₂F₃NO: C, 65.98; H, 4.15; N, 4.81%.

7-Acetyl-3-chloro-8-methyl-8-phenylbicyclo[**4.2.0**]**-7-azaoct-1,3,5-triene (3f).** A similar reaction of **2f** with *n*-Bu₃SnH at room temperature overnight gave **3f**: mp 158–161 °C (hexane–Et₂O); IR (KBr disk) 1643 and 1599 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.96 (3H, s), 2.14 (3H, s), 6.99 (1H, d, *J* = 2.3 Hz), 7.10 (1H, d, *J* = 8.7 Hz), 7.25 (1H, dd, *J* = 8.7, 2.3 Hz), and 7.30–7.35 (5H, m); MS (EI) *m*/*z* (%) 271 (M⁺, 32) and 228 (100). Found: C, 70.64; H, 5.09; N, 4.92%. Calcd for C₁₆H₁₄ClNO: C, 70.72; H, 5.19; N, 5.15%.

7-Acetyl-8-methyl-8-(phenylthiomethyl)bicyclo[4.2.0]-7-azaoct-1,3,5-triene (4a). To a stirred suspension of NaH (60% in oil, 29 mg, 0.73 mmol) in DMF (2 mL) at 0 °C was added PhSH (80 mg, 0.73 mmol) dropwise. After stirring for 1 h, a solution of 2a (0.20 g, 0.66 mmol) in DMF (2 mL) was added dropwise. After stirring for 5 h at the same temperature, the resulting mixture was treated with saturated aqueous NH₄Cl (15 mL) and organic materials were extracted with Et₂O three times (10 mL each). The combined extracts were washed with water twice and then brine once, and dried over anhydrous Na₂SO₄. Evaporation of the solvent gave a residue, which was purified by preparative TLC on SiO₂ to afford **4a** (0.10 g, 55%); R_f 0.24 (3:1 hexane-AcOEt); IR (neat) 1645 and 1602 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.77 (3H, s), 1.88 (3H, s), 3.25 (1H, d, J = 14.2 Hz), 3.44 (1H, d, J = 14.2 Hz), 7.05 (1H, dd, J = 8.7, 1.9 Hz), 7.10-7.18 (3H, m), 7.20-7.24 (3H, m), and 7.29 (2H, d, J = 7.3 Hz); MS (EI) m/z (%) 283 (M⁺, 3.0) and 160 (100). Found: C, 71.99; H, 6.10; N, 5.01; S, 11.15%. Calcd for C₁₇H₁₇NOS: C, 72.05; H, 6.05; N, 4.94; S, 11.32%.

7-Benzoyl-8-methyl-8-(phenylthiomethyl)bicyclo[4.2.0]-7-azaoct-1,3,5-triene (4c). Prepared in a manner similar to that described above for **4a**; R_f 0.40 (5:1 hexane–AcOEt); IR (neat) 1626 and 1599 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.87 (3H, s), 3.38 (1H, d, J = 13.7 Hz), 3.56 (1H, d, J = 13.7 Hz), 7.08 (1H, tt, J = 7.3, 2.3 Hz), 7.12–7.19 (4H, m), 7.24 (2H, dd, J = 7.8, 1.3 Hz), 7.30–7.32 (2H, m), 7.40 (2H, t, J = 7.8 Hz), 7.47 (1H, tt, J = 7.3, 2.3 Hz), and 8.09 (2H, dd, J = 6.9, 1.8 Hz); MS (EI) m/z (%) 345 (M⁺, 5.1) and 222 (100). Found: C, 76.28; H, 5.55; N, 3.95; S 9.16%. Calcd for C₂₂H₁₉NOS: C, 76.49; H, 5.54; N, 4.05; S, 9.28%.

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